



# Multi-input Schrödinger equation: controllability, tracking, and application to the quantum angular momentum

Ugo Boscain, Marco Caponigro, Mario Sigalotti

## ► To cite this version:

Ugo Boscain, Marco Caponigro, Mario Sigalotti. Multi-input Schrödinger equation: controllability, tracking, and application to the quantum angular momentum. *Journal of Differential Equations*, 2014, 256 (11), pp.3524-3551. 10.1016/j.jde.2014.02.004 . hal-01097161v2

**HAL Id: hal-01097161**

**<https://hal.science/hal-01097161v2>**

Submitted on 1 Sep 2016

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Multi-input Schrödinger equation: controllability, tracking, and application to the quantum angular momentum<sup>☆</sup>

Ugo Boscain

*CNRS, CMAP, École Polytechnique, Palaiseau, France, & Team GECO, INRIA Saclay*

Marco Caponigro

*Conservatoire National des Arts et Métiers, Équipe M2N, Paris, France*

Mario Sigalotti

*INRIA Saclay, Team GECO & CMAP, École Polytechnique, Palaiseau, France*

---

## Abstract

We present a sufficient condition for approximate controllability of the bilinear discrete-spectrum Schrödinger equation in the multi-input case. The controllability result extends to simultaneous controllability, approximate controllability in  $H^s$ , and tracking in modulus. The sufficient condition is more general than those present in the literature even in the single-input case and allows the spectrum of the uncontrolled operator to be very degenerate (e.g. to have multiple eigenvalues or equal gaps among different pairs of eigenvalues). We apply the general result to a rotating polar linear molecule, driven by three orthogonal external fields. A remarkable property of this model is the presence of infinitely many degeneracies and resonances in the spectrum.

*Keywords:* Quantum control, bilinear Schrödinger equation, Galerkin approximations, quantum angular momentum.

---

## 1. Introduction

In this paper we study the controllability and the tracking problem for the multi-input bilinear Schrödinger equation

$$i\frac{d\psi}{dt}(t) = (H_0 + u_1(t)H_1 + \dots + u_p(t)H_p)\psi(t) \quad (1)$$

---

<sup>☆</sup>This research has been supported by the European Research Council, ERC StG 2009 “GeCoMethods”, contract number 239748, by the ANR project GCM, program “Blanc”, project number NT09-504490

*Email addresses:* ugo.boscain@polytechnique.edu (Ugo Boscain), marco.caponigro@cnam.fr (Marco Caponigro), mario.sigalotti@inria.fr (Mario Sigalotti)

where  $H_0, \dots, H_p$  are self-adjoint operators on a Hilbert space  $\mathcal{H}$  and the drift Schrödinger operator  $H_0$  (the *internal Hamiltonian*) has discrete spectrum. The control functions  $u_1(\cdot), \dots, u_p(\cdot)$ , representing external fields, are real-valued and  $\psi(\cdot)$  takes values in the unit sphere of  $\mathcal{H}$ .

The controllability of system (1) is a well-established topic when the state space  $\mathcal{H}$  is finite-dimensional (see for instance [D'A08] and reference therein), thanks to general controllability methods for left-invariant control systems on compact Lie groups ([Bro72, JS72, JK81, GB82, EAGK96]).

When  $\mathcal{H}$  is infinite-dimensional and the operators  $H_1, \dots, H_p$  are bounded, it is known that the bilinear Schrödinger equation is not exactly controllable (see [BMS82, Tur00]). Nevertheless, weaker controllability properties, such as approximate controllability or controllability between eigenstates of the internal Hamiltonian  $H_0$  (which are the most relevant physical states), may hold. In certain cases, when  $\mathcal{H}$  is a function space on a subset of  $\mathbb{R}$ , a description of reachable sets has been provided (see [BC06, BL10]). In  $\mathbb{R}^d$ ,  $d > 1$ , or for more general situations, the exact description of the reachable set seems a difficult task and at the moment only approximate controllability results are available. Most of them have been proved in the single-input case (see, in particular, [CMSB09, Mir09, Ner09, Ner10, BN10, BCCS12, NN12]). They are based on sufficient conditions for controllability that are generic [PS10, MS10, Ner10] even in the case  $p = 1$ . Nevertheless, in many examples these conditions cannot be directly applied or controllability fails to hold, as a consequence of the symmetries of the system. Symmetries can induce degeneracies in the spectrum (e.g. multiple eigenvalues or presence of identical spectral gaps) and reduce the coupling of eigenstates via the control. This happens, for instance, for a planar rotating molecule controlled by one external field only [BCCS12, Section 8], which is not (approximately) controllable.

Using more than one input opens new possibility for control.

Multi-input controllability results have been obtained for specific systems [EP09, BBR10] and some general approximate controllability results between eigenfunctions have been proved via adiabatic methods [AB05, BCMS12]. The first multi-input result via Lie-algebraic methods is given in [BCCS12, Section 8], where the spectral degeneracies of the planar rotating molecule have been tackled by associating with every 1-dimensional slice of the set of admissible controls an invariant subspace of the state space  $\mathcal{H}$  on which the single-input controllability result applies. However, such a technique does not apply in more general cases. In the case of a rotating rigid symmetric 3D molecule, the application of this method is obstructed by the fact that eigenspaces may have arbitrarily large dimension.

In this paper, we present a sufficient condition for controllability of the discrete-spectrum bilinear Schrödinger equation which applies even when the spectrum of the internal Hamiltonian  $H_0$  is very degenerate. The results fully exploit the presence of more than one control and extend to simultaneous controllability, approximate controllability in  $H^s$ , and tracking in modulus (or *m-tracking*; for precise definitions see Section 2). Proving that a system is an *m-tracker* is a crucial issue when dealing with dissipative levels. A common

strategy is to neglect the dissipativity of the level in the mathematical model and to keep its population as low as possible during the transition (see for instance the STIRAP model [CH90, VHBB01, BCG<sup>+</sup>02]).

The result presented in this paper is more general than those in the literature even in the single-input case. Consider, for instance, the Laplace–Dirichlet operator on a compact interval  $\Omega$  of  $\mathbb{R}$  with a control term of the type  $(H_1\psi)(x) = x\psi(x)$ ,  $x \in \Omega$  (see [BC06]): in [BCCS12], approximate simultaneous controllability of this model has been proved by breaking the degeneracies between spectral gaps through perturbation techniques. Here we prove the approximate simultaneous controllability and m-tracking without perturbation arguments. The advantage is that the constructive proof of the main result translates into an explicit motion-planning algorithm [CBCS11].

### 1.1. Brief description of the general results

The main result of the paper is a sufficient condition for approximate simultaneous controllability which we call the Lie–Galerkin Control Condition (see Definition 2.5).

Roughly speaking, both the sufficient condition proposed in [BCCS12] and the one presented here are based on the idea of driving the system with control laws that are in resonance with spectral gaps of the internal Hamiltonian  $H_0$ . However, while in [BCCS12] the only actions on the system obtained by resonance that are exploited for the controllability are those corresponding to elementary transitions between two eigenstates, no such a restriction is imposed in the Lie–Galerkin Control Condition (see Section 2.5).

The Lie–Galerkin Control Condition ensures strong controllability properties for the Galerkin approximations: it provides controllability for a fixed Galerkin approximation while avoiding the transfer of population to higher energy levels for higher-order Galerkin approximations. This yields estimates on the difference between the dynamics of the finite-dimensional Galerkin approximation and the original infinite-dimensional system. The Lie–Galerkin Control Condition also ensures a bound on the  $L^1$  norm of the control achieving controllability between finite combinations of eigenstates, which is uniform with respect to the prescribed tolerance.

Under the Lie–Galerkin Tracking Condition, a slight modification of the Lie–Galerkin Control Condition, we can prove that any trajectory can be tracked in modulus (see Theorem 2.8).

Following [BCC13], the Lie–Galerkin Control Condition, under the additional assumption that the system is  $s$ -weakly coupled (see Definition 2.11), implies that the system is approximately controllable in  $H^{s/2}$  (see Theorem 2.12).

### 1.2. Application to the quantum angular momentum

Rotational molecular dynamics constitute one of the most important examples of quantum systems on an infinite-dimensional Hilbert space and with discrete spectrum. Molecular orientation and alignment are well-established topics in the quantum control of molecular dynamics both from the experimental and the theoretical point of view (see [SS03, SKA<sup>+</sup>04, SH06] and references

therein). For linear molecules driven by linearly polarized laser fields in gas phase, alignment means an increased probability direction along the polarization axis whereas orientation requires in addition the same direction as the polarization vector. A large amount of numerical simulations have been carried on in this area but the mathematical part is not yet fully understood.

We focus in this paper on the control of the orientation of a rigid linear molecule in  $\mathbb{R}^3$  by external fields. The corresponding controlled Schrödinger equation is defined on the unit sphere  $S^2$ . We show that the system driven by three fields along the three axes is approximately controllable for arbitrarily small controls.

Up to normalization of physical quantities (in particular, in units such that  $\hbar = 1$ ), the dynamics are modeled by the equation

$$i \frac{\partial \psi(\theta, \varphi, t)}{\partial t} = -\Delta \psi(\theta, \varphi, t) + (u_1(t) \sin \theta \cos \varphi + u_2(t) \sin \theta \sin \varphi + u_3(t) \cos \theta) \psi(\theta, \varphi, t), \quad (2)$$

where  $\theta, \varphi$  are the spherical coordinates, which are related to the Euclidean coordinates through the identities

$$x = \sin \theta \cos \varphi, \quad y = \sin \theta \sin \varphi, \quad z = \cos \theta,$$

while  $\Delta$  is the Laplace–Beltrami operator on the sphere  $S^2$  (called in this context the *angular momentum operator*), i.e.,

$$\Delta = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2}.$$

The wavefunction  $\psi$  evolves in the unit sphere  $\mathcal{S}$  of  $\mathcal{H} = L^2(S^2, \mathbb{C})$ .

As a consequence of the general multi-input result presented in Section 2 we have that (2) is approximately controllable with arbitrarily small controls. A stronger statement, including simultaneous controllability in  $H^s$  and tracking in modulus, is given in Section 3.

**Theorem 1.1.** *For every  $\psi^0, \psi^1$  belonging to  $\mathcal{S}$  and every  $\varepsilon, \delta > 0$ , there exist  $T > 0$  and  $u \in L^\infty([0, T], [0, \delta]^3)$ , such that the solution  $\psi(\cdot)$  of equation (2), corresponding to the control  $u$  and with initial condition  $\psi_0$ , satisfies  $\|\psi^1 - \psi(T)\| < \varepsilon$ .*

There are two main difficulties preventing the application of previous results in the literature to this system. Firstly, we deal here with several control parameters, while those general results were specific to the single-input case. Notice that, because of symmetry obstructions, equation (2) is not controllable with only two of the three controls  $u_1, u_2, u_3$ . Secondly, the general theory developed in [CMSB09, Ner10, BCCS12] is based on nonresonance conditions on the spectrum of the internal Hamiltonian. The Laplace–Beltrami operator on  $S^2$ , however, has a severely degenerate spectrum, since the  $\ell$ -th eigenvalue  $-\ell(\ell+1)$  has multiplicity  $2\ell+1$ . A perturbation technique has been proposed

in [CMSB09], in order to overcome resonance relations in the spectrum of the drift. The technique was applied in [BCM<sup>+</sup>09] to the case of the orientation of a molecule confined in a plane driven by one control. The planar case is already technically challenging and a generalization of the same technique to the case of three controls in 3D seems hard to achieve.

### 1.3. Structure of the paper

The paper is organized as follows: in the next section we present the general multi-input abstract framework and the main abstract results (Theorems 2.6, 2.8, and 2.12). In Section 3 we apply them to system (2). The proofs of Theorems 2.6, 2.8, and 2.12 are contained, respectively, in Sections 4, 5, and 6.

## 2. Framework and main results

Let  $p \in \mathbb{N}$ ,  $\delta > 0$ , and  $U = U_1 \times \cdots \times U_p$  with either  $U_j = [0, \delta]$  or  $U_j = [-\delta, \delta]$ .

**Definition 2.1.** Let  $\mathcal{H}$  be an infinite-dimensional Hilbert space with scalar product  $\langle \cdot, \cdot \rangle$  and  $A, B_1, \dots, B_p$  be (possibly unbounded) skew-adjoint operators on  $\mathcal{H}$ , with domains  $D(A), D(B_1), \dots, D(B_p)$ . Let us introduce the controlled equation

$$\frac{d\psi}{dt}(t) = (A + u_1(t)B_1 + \cdots + u_p(t)B_p)\psi(t), \quad u(t) \in U. \quad (3)$$

We say that  $A$  satisfies (A1) if the following assumption is true:

(A1)  $A$  has discrete spectrum with infinitely many distinct eigenvalues (possibly degenerate).

Denote by  $\Phi$  a Hilbert basis  $(\phi_k)_{k \in \mathbb{N}}$  of  $\mathcal{H}$  made of eigenvectors of  $A$  associated with the family of eigenvalues  $(i\lambda_k)_{k \in \mathbb{N}}$  and let  $\mathcal{L}$  be the set of finite linear combinations of eigenstates, that is,

$$\mathcal{L} = \bigcup_{k \in \mathbb{N}} \text{span}\{\phi_1, \dots, \phi_k\}.$$

We say that  $(A, B_1, \dots, B_p, U, \Phi)$  satisfies (A) if  $A$  satisfies (A1) and the following assumptions hold:

(A2)  $\phi_k \in D(B_j)$  for every  $k \in \mathbb{N}, j = 1, \dots, p$ ;

(A3)  $A + u_1 B_1 + \cdots + u_p B_p : \mathcal{L} \rightarrow \mathcal{H}$  is essentially skew-adjoint for every  $u \in U$ .

If  $(A, B_1, \dots, B_p, U, \Phi)$  satisfies (A) then, for every  $(u_1, \dots, u_p) \in U$ ,  $A + u_1 B_1 + \cdots + u_p B_p$  generates a subgroup  $e^{t(A + u_1 B_1 + \cdots + u_p B_p)}$  of the group of unitary operators  $\mathbf{U}(\mathcal{H})$ . It is therefore possible to define the propagator  $\Upsilon_T^u$  at time  $T$  of system (2) associated with a  $p$ -uple of piecewise constant controls  $u(\cdot) = (u_1(\cdot), \dots, u_p(\cdot))$  by composition of flows of the type  $e^{t(A + u_1 B_1 + \cdots + u_p B_p)}$ . If, moreover,  $B_1, \dots, B_p$  are bounded operators then the definition can be extended by continuity to every  $L^\infty$  control law (see [BMS82, Theorem 2.5]).

**Definition 2.2.** Let  $(A, B_1, \dots, B_p, U, \Phi)$  satisfy (A). We say that (3) is *approximately controllable* if for every  $\psi_0, \psi_1$  in the unit sphere of  $\mathcal{H}$  and every  $\varepsilon > 0$  there exists a piecewise constant control function  $u : [0, T] \rightarrow U$  such that  $\|\psi_1 - \Upsilon_T^u(\psi_0)\| < \varepsilon$ .

**Definition 2.3.** Let  $(A, B_1, \dots, B_p, U, \Phi)$  satisfy (A). We say that (3) is *approximately simultaneously controllable* if for every  $r$  in  $\mathbb{N}$ ,  $\psi_1, \dots, \psi_r$  in  $\mathcal{H}$ ,  $\hat{\Upsilon}$  in  $\mathbf{U}(\mathcal{H})$ , and  $\varepsilon > 0$  there exists a piecewise constant control  $u : [0, T] \rightarrow U$  such that

$$\|\hat{\Upsilon}\psi_k - \Upsilon_T^u\psi_k\| < \varepsilon, \quad k = 1, \dots, r.$$

If, moreover, for every  $\psi_1, \dots, \psi_r \in \mathcal{L}$  and  $\hat{\Upsilon} \in \mathbf{U}(\mathcal{H})$  such that  $\hat{\Upsilon}\psi_1, \dots, \hat{\Upsilon}\psi_r \in \mathcal{L}$ , there exists  $K > 0$  (not depending on  $\varepsilon$ ) such that  $u$  can be chosen to satisfy, in addition,  $\|u\|_{L^1} \leq K$ , we say that (3) is  *$L^1$ -bounded approximately simultaneously controllable*.

This last definition of controllability with *a priori* bound on the  $L^1$ -norm of the control achieving controllability has been observed in preceding works [BCCS12, Cha12]. It implies a stronger controllability property as discussed in Section 2.4.

Because of the presence of a drift (the internal Hamiltonian) and of the boundedness of the controls, it is not possible in general to track, with arbitrarily precision, an unfeasible curve in  $\mathcal{S}$ . We introduce the notion of an m-tracker, that is, a system for which any given curve can be tracked up to phases (both for a single initial condition and in the spirit of simultaneous control). This definition makes sense from the physical point of view, since tracking up to phases means imposing the population of all energy levels of  $H_0$  along the evolution.

The identification up to phases of elements of  $\mathcal{H}$  in the basis  $\Phi = (\phi_k)_{k \in \mathbb{N}}$  can be accomplished by the projection

$$\mathfrak{M} : \psi \mapsto \sum_{k \in \mathbb{N}} |\langle \phi_k, \psi \rangle| \phi_k.$$

**Definition 2.4.** Let  $(A, B_1, \dots, B_p, U, \Phi)$  satisfy (A). We say that (3) is a *m-tracker* if, for every  $r$  in  $\mathbb{N}$ ,  $\psi_1, \dots, \psi_r$  in  $\mathcal{H}$ ,  $\hat{\Upsilon} : [0, T] \rightarrow \mathbf{U}(\mathcal{H})$  continuous with  $\hat{\Upsilon}_0 = \text{Id}_{\mathcal{H}}$ , and  $\varepsilon > 0$ , there exist an invertible increasing continuous function  $\tau : [0, T] \rightarrow [0, T_\tau]$  and a piecewise constant control  $u : [0, T_\tau] \rightarrow U$  such that

$$\|\mathfrak{M}(\hat{\Upsilon}_t\psi_k) - \mathfrak{M}(\Upsilon_{\tau(t)}^u\psi_k)\| < \varepsilon, \quad k = 1, \dots, r,$$

for every  $t \in [0, T_\tau]$ .

### 2.1. Notation

For every  $n$  in  $\mathbb{N}$ , define the orthogonal projection

$$\pi_n : \mathcal{H} \ni \psi \mapsto \sum_{k=1}^n \langle \phi_k, \psi \rangle \phi_k \in \mathcal{H}.$$

Given a linear operator  $Q$  on  $\mathcal{H}$  we identify the linear operator  $\pi_n Q \pi_n$  preserving  $\text{span}\{\phi_1, \dots, \phi_n\}$  with its  $n \times n$  complex matrix representation with respect to the basis  $(\phi_1, \dots, \phi_n)$ . We define

$$A^{(n)} = \pi_n A \pi_n \quad \text{and} \quad B_j^{(n)} = \pi_n B_j \pi_n,$$

for every  $j = 1, \dots, p$ .

Let us introduce the set  $\Sigma_n$  of spectral gaps associated with the  $n$ -dimensional Galerkin approximation as

$$\Sigma_n = \{|\lambda_l - \lambda_k| \mid l, k = 1, \dots, n\}.$$

For every  $\sigma \geq 0$ , every  $m \in \mathbb{N}$ , and every  $m \times m$  matrix  $M$ , let

$$\mathcal{E}_\sigma(M) = (M_{l,k} \delta_{\sigma, |\lambda_l - \lambda_k|})_{l,k=1}^m,$$

where  $\delta_{j,k} = 1$  if and only if  $j = k$  and  $\delta_{j,k} = 0$  otherwise. The  $n \times n$  matrix  $\mathcal{E}_\sigma(B_j^{(n)})$ ,  $j = 1, \dots, p$ , corresponds to the “activation” in  $B_j^{(n)}$  of the spectral gap  $\sigma$ : every element is 0 except the  $(l, k)$ -elements such that  $|\lambda_l - \lambda_k| = \sigma$ . (It reflects the action of the convexification procedure detailed in Section 4.4, which sets to zero all the matrix elements  $(B_j^{(n)})_{l,k}$  for which  $|\lambda_l - \lambda_k| \neq \sigma$ .)

Define

$$\begin{aligned} \Xi_n = & \{(\sigma, j) \in \Sigma_n \times \{1, \dots, p\} \mid \\ & \exists M \in \mathfrak{u}(n) \text{ s.t. } \mathcal{E}_\sigma(B_j^{(N)}) = \left( \begin{array}{c|c} M & 0 \\ \hline 0 & * \end{array} \right) \text{ for every } N > n\}. \end{aligned} \quad (4)$$

The matrices  $\mathcal{E}_\sigma(B_j^{(n)})$  for  $(\sigma, j) \in \Xi_n$  correspond to “compatible dynamics” for the  $n$ -dimensional Galerkin approximation (*compatible*, that is, with higher-dimensional Galerkin approximations).

## 2.2. Controllability results

Let

$$\begin{aligned} \mathcal{V}_n^0 = & \left\{ A^{(n)} \right\} \cup \left\{ \mathcal{E}_\sigma(B_j^{(n)}) \mid (\sigma, j) \in \Xi_n \text{ and } j \text{ is such that } (0, j) \in \Xi_n \right\} \\ & \cup \left\{ \mathcal{E}_\sigma(B_j^{(n)}) \mid (\sigma, j) \in \Xi_n, \sigma \neq 0, U_j = [-\delta, \delta] \right\}. \end{aligned}$$

The family  $\mathcal{V}_n^0$  is obtained by collecting compatible dynamics coming from the convexification procedure mentioned in the previous section. It also contains matrix  $A^{(n)}$  obtained by the truncation of the drift  $A$ , which is itself the drift of the Galerkin approximation of order  $n$ . The collections of the “compatible dynamics”  $\mathcal{E}_\sigma(B_j^{(n)})$  is restricted to the indices  $j$  such that  $(0, j) \in \Xi_n$  or such that  $U_j = [-\delta, \delta]$ . These conditions allow to decouple the contribution of the drift in the convexification procedure, as detailed in Section 4.6.



**Definition 2.5.** Let  $(A, B_1, \dots, B_p, U, \Phi)$  satisfy (A). We say that the *Lie-Galerkin Control Condition* holds if for every  $n_0 \in \mathbb{N}$  there exists  $n > n_0$  such that

$$\text{Lie}\mathcal{V}_n^0 \supseteq \mathfrak{su}(n). \quad (5)$$

**Theorem 2.6** (Abstract multi-input controllability result). *Assume that (A) holds true. If the Lie-Galerkin Control Condition holds then the system*

$$\dot{x} = (A + u_1 B_1 + \dots + u_p B_p)x, \quad u \in U,$$

*is  $L^1$ -bounded approximately simultaneously controllable.*

### 2.3. Tracking results

For every  $\xi \in S^1 \subset \mathbb{C}$ , consider the matrix operator  $J_\xi$  such that

$$(J_\xi(M))_{j,k} = \begin{cases} \xi M_{j,k} & \text{if } \lambda_j < \lambda_k, \\ 0 & \text{if } \lambda_j = \lambda_k, \\ \bar{\xi} M_{j,k} & \text{if } \lambda_j > \lambda_k. \end{cases}$$

Let

$$\mathcal{V}_n = \left\{ J_\xi(\mathcal{E}_\sigma(B_j^{(n)})) \mid (\sigma, j) \in \Xi_n, \sigma \neq 0, \xi \in S^1 \right\}. \quad (6)$$

Notice that  $\mathcal{V}_n \subset \mathfrak{su}(n)$ .

**Definition 2.7.** Let  $(A, B_1, \dots, B_p, U, \Phi)$  satisfy (A). We say that the *Lie-Galerkin Tracking Condition* holds if for every  $n_0 \in \mathbb{N}$  there exists  $n > n_0$  such that

$$\text{Lie}\mathcal{V}_n = \mathfrak{su}(n). \quad (7)$$

**Theorem 2.8** (Abstract multi-input tracking result). *Let  $U_j = [-\delta, \delta]$  for some  $\delta > 0$  and every  $j = 1, \dots, p$ . Assume that (A) holds true. If the Lie-Galerkin Tracking Condition holds then the system*

$$\dot{x} = (A + u_1 B_1 + \dots + u_p B_p)x, \quad u \in U,$$

*is a  $m$ -tracker.*

**Remark 2.9.** If  $U_j = [-\delta, \delta]$  for every  $j = 1, \dots, p$ , then the Lie-Galerkin Tracking Condition implies the Lie-Galerkin Control Condition, as it follows from the relations

$$\left[ A^{(n)}, \mathcal{E}_\sigma(B_j^{(n)}) \right] = \sigma J_i(\mathcal{E}_\sigma(B_j^{(n)})) \quad \text{and} \quad J_1(\mathcal{E}_\sigma(B_j^{(n)})) = \mathcal{E}_\sigma(B_j^{(n)}),$$

for  $\sigma \neq 0$ .

#### 2.4. Controllability in higher norms

We define for  $s > 0$ ,

$$|A|^s \psi = \sum_{n \in \mathbb{N}} |\lambda_n|^s \langle \phi_n, \psi \rangle \phi_n,$$

for every  $\psi$  belonging to

$$D(|A|^s) = \left\{ \psi \in \mathcal{H} \mid \sum_{n \in \mathbb{N}} |\lambda_n|^{2s} |\langle \phi_n, \psi \rangle|^2 < +\infty \right\}.$$

For every  $\psi \in D(|A|^s)$  we can define the  $|A|^s$ -norm (or simply  $s$ -norm) of  $\psi$  by  $\|\psi\|_s = \| |A|^s \psi \|$ . If  $A$  is the Laplace–Dirichlet operator on some bounded domain of  $\mathbb{R}^n$  then the  $s$ -norm is equivalent to the  $H^{2s}$ -norm on  $D(|A|^s)$ .

**Definition 2.10.** Let  $(A, B_1, \dots, B_p, U, \Phi)$  satisfy Assumption (A) and let  $s > 0$ . System (3) is *approximately simultaneously controllable* (respectively *approximately controllable*) for the  $s$ -norm if, for every  $\varepsilon > 0$ ,  $r \in \mathbb{N}$  (respectively  $r = 1$ ),  $\psi_1, \dots, \psi_r$  in  $D(|A|^s)$ , and  $\hat{\Upsilon} \in \mathbf{U}(\mathcal{H})$  such that  $\hat{\Upsilon}\psi_1, \dots, \hat{\Upsilon}\psi_r \in D(|A|^s)$  there exists a piecewise constant function  $u_\varepsilon : [0, T_\varepsilon] \rightarrow \mathbb{R}$  such that

$$\|\hat{\Upsilon}\psi_j - \Upsilon_{T_\varepsilon}^{u_\varepsilon} \psi_j\|_s < \varepsilon,$$

for every  $j = 1, \dots, r$ .

We say that  $(A, B_1, \dots, B_p, U, \Phi)$  satisfies (A') if it satisfies (A) and the following additional assumptions hold:

(A4) the operator  $i(A + u_1 B_1 + \dots + u_p B_p)$  is bounded from below for every  $u \in \mathbb{R}^p$ ;

(A5) the sequence  $(\lambda_k)_{k \in \mathbb{N}}$  is non-increasing and unbounded.

**Definition 2.11.** Let  $(A, B_1, \dots, B_p, U, \Phi)$  satisfy Assumption (A') and let  $s > 0$ . Then  $(A, B_1, \dots, B_p)$  is *s-weakly-coupled* if  $D(|A + u_1 B_1 + \dots + u_p B_p|^{s/2}) = D(|A|^{s/2})$  for every  $u \in \mathbb{R}^p$  and there exists  $C$  such that

$$|\Re \langle |A|^s \psi, B_j \psi \rangle| \leq C |\langle |A|^s \psi, \psi \rangle|,$$

for every  $j = 1, \dots, p$ ,  $\psi \in D(|A|^s)$ .

The following result is a consequence of [BCC13, Proposition 2] and can be obtained by adapting the arguments of [BCC13, Proposition 5]. We provide a proof in Section 6.

**Theorem 2.12.** Let  $(A, B_1, \dots, B_p, U, \Phi)$  satisfy Assumption (A') and  $(A, B_1, \dots, B_p)$  be  $s$ -weakly coupled for some  $s > 0$ . If (3) is  $L^1$ -bounded approximately simultaneously controllable then it is approximately simultaneously controllable for the  $s/2$ -norm.

As a direct consequence we have the following result generalizing [BCC13, Proposition 5].

**Corollary 2.13.** *Let  $(A, B_1, \dots, B_p, U, \Phi)$  satisfy Assumption  $(\mathbb{A}')$  and  $(A, B_1, \dots, B_p)$  be  $s$ -weakly coupled for some  $s > 0$ . If the Lie–Galerkin Control Condition holds then system (3) is approximately simultaneously controllable for the  $s/2$ -norm.*

### 2.5. Example: the infinite potential well

We present the case of a particle confined in the interval  $(-\pi/2, \pi/2)$  as a toy model to compare the results in [BCCS12] and Theorem 2.8 in the case of a single-input system. The model was extensively studied by several authors in the last decade and it has been the first quantum system for which a positive controllability result was obtained (see [BC06]). In [BCCS12] an approximate simultaneous controllability result was obtained via geometric methods and using perturbations techniques.

The Schrödinger equation reads

$$i \frac{\partial \psi}{\partial t} = -\frac{\partial^2 \psi}{\partial x^2} - u(t)x\psi(x, t), \quad (8)$$

with the boundary conditions  $\psi(-\pi/2, t) = \psi(\pi/2, t) = 0$  for every  $t \in \mathbb{R}$ . The controls  $u(\cdot)$  are piecewise constant with values in  $U = [-\delta, \delta]$  for some  $\delta > 0$ .

In this case  $\mathcal{H}$  is the space  $L^2((-\pi/2, \pi/2), \mathbb{C})$  endowed with the Hermitian product  $\langle \psi_1, \psi_2 \rangle = \int_{-\pi/2}^{\pi/2} \overline{\psi_1(x)} \psi_2(x) dx$ . The operators  $A$  and  $B = B_1$  are defined by  $A\psi = i \frac{\partial^2 \psi}{\partial x^2}$  for every  $\psi$  in  $D(A) = (H_2 \cap H_0^1)((-\pi/2, \pi/2), \mathbb{C})$  and  $B\psi = ix\psi$ . A complete set of eigenfunctions of  $A$  associated with the eigenvalues  $i\lambda_k = -ik^2$ ,  $k \in \mathbb{N}$  is given by

$$\phi_k(x) = \begin{cases} \sqrt{\frac{2}{\pi}} \cos(kx) & \text{when } k \text{ is odd,} \\ \sqrt{\frac{2}{\pi}} \sin(kx) & \text{when } k \text{ is even,} \end{cases} \quad k \in \mathbb{N}.$$

Notice that

$$\langle \phi_j, B\phi_k \rangle \neq 0,$$

if and only if  $j + k$  is odd. In particular  $J_\xi(\mathcal{E}_\sigma(B^{(n)})) = \mathcal{E}_\sigma(B^{(n)})$  for every  $\xi \in S^1$ ,  $n \in \mathbb{N}$ , and  $\sigma \in \Sigma_n$ .

We prove by induction on  $n \geq 2$  that  $\text{Lie}\mathcal{V}_n = \mathfrak{su}(n)$ , and hence that the Lie–Galerkin Tracking Condition is fulfilled. Notice that, for every  $k = 2, \dots, n$ , the spectral gap  $|\lambda_k - \lambda_{k-1}| = 2k - 1$  belongs to  $\Sigma_n$  and that the  $(j, l)$ -th element of the matrix  $\mathcal{E}_{2k-1}(B^{(n)})$  is zero for  $j \leq n$  and  $l \geq n + 1$ , since

$$l^2 - j^2 \geq (n + 1)^2 - n^2 = 2n + 1 > 2k - 1.$$

Hence  $\mathcal{E}_{2k-1}(B^{(n)}) \in \mathcal{V}_n$  for  $k = 2, \dots, n$ . We prove the claim by showing that

$$\text{Lie}\left(\{\mathcal{E}_{2k-1}(B^{(n)}) \mid k = 1, \dots, n\}\right) = \mathfrak{su}(n). \quad (9)$$

For  $n = 2$ , the matrices  $\mathcal{E}_3(B^{(2)}) = \begin{pmatrix} 0 & b_{12} \\ -\bar{b}_{12} & 0 \end{pmatrix}$  and  $J_i(\mathcal{E}_3(B^{(2)}))$  generate  $\mathfrak{su}(2)$  because  $b_{12} \neq 0$ .

Now assume that

$$\text{Lie} \left( J_\xi(\{\mathcal{E}_{2k-1}(B^{(n-1)}) \mid \xi \in S^1, k = 2, \dots, n-1\}) \right) = \mathfrak{su}(n-1),$$

and let us prove (9). The matrices  $J_\xi(\mathcal{E}_{2k-1}(B^{(n)}))$ ,  $\xi \in S^1$ ,  $k = 2, \dots, n-1$ , generate the subalgebra of matrices in  $\mathfrak{su}(n)$  with zero elements in the  $n$ -th row and  $n$ -th column. In particular, there exists

$$M \in \text{Lie} \left( \{J_\xi(\mathcal{E}_{2k-1}(B^{(n)})) \mid \xi \in S^1, k = 2, \dots, n-1\} \right)$$

such that  $M + \mathcal{E}_{2n-1}(B^{(n)})$  has the only two nonzero elements in the positions  $(n-1, n)$  and  $(n, n-1)$ . So

$$\begin{aligned} & \text{Lie}(\{J_\xi(\mathcal{E}_{2k-1}(B^{(n)})) \mid \xi \in S^1, k = 2, \dots, n\}) \\ & \supset \text{Lie} \left( \{J_\xi(\mathcal{E}_{2k-1}(B^{(n)})) \mid \xi \in S^1, k = 2, \dots, n-1\} \cup \{M + \mathcal{E}_{2n-1}(B^{(n)})\} \right) \\ & = \mathfrak{su}(n). \end{aligned}$$

Therefore, thanks to Theorems 2.6 and 2.8, system (8) is approximately simultaneously controllable and an m-tracker.

### 3. The 3D molecule

Let us go back to the system for the orientation of a linear molecule presented in the introduction, that is,

$$i\hbar\dot{\psi} = -\Delta\psi + (u_1 \cos \theta + u_2 \cos \varphi \sin \theta + u_3 \sin \varphi \sin \theta)\psi, \quad (10)$$

where  $\psi(t) \in \mathcal{H} = L^2(S^2, \mathbb{C})$ .

A basis of eigenvectors of the Laplace–Beltrami operator  $\Delta$  is given by the spherical harmonics  $Y_\ell^m(\theta, \varphi)$ , which satisfy

$$\Delta Y_\ell^m(\theta, \varphi) = -\ell(\ell+1)Y_\ell^m(\theta, \varphi).$$

The spectrum of  $A = i\Delta$  is  $\{-i\ell(\ell+1) \mid \ell \in \mathbb{N}\}$ . Each eigenvalue  $-i\ell(\ell+1)$  is of finite multiplicity  $2\ell+1$ . Therefore  $A$  satisfies Assumptions (A1) and (A5). Using the notations of the preceding sections, we set  $B_1$ ,  $B_2$ ,  $B_3$  to be the multiplication operators by  $-i \cos \varphi \sin \theta$ ,  $-i \sin \varphi \sin \theta$ ,  $-i \cos \theta$ , respectively. Since  $B_1$ ,  $B_2$ ,  $B_3$  are bounded, conditions (A2), (A3), and (A4) hold. Hence (A') is satisfied. Moreover, as proved in [BCC13, Proposition 8], (10) is  $s$ -weakly coupled for every  $s > 0$ . The main goal of this section is to prove that system (10) satisfies the Lie–Galerkin Tracking Condition. As a consequence, we obtain the following result, whose corollary is Theorem 1.1.

**Theorem 3.1.** *System (10) is:*

- (i)  $L^1$ -bounded approximately simultaneously controllable,
- (ii) approximately simultaneously controllable in  $H^s$  for every  $s > 0$ ,
- (iii) a  $m$ -tracker.

Using classical identities for Legendre polynomials and trigonometric relations, one can prove that

$$\langle Y_\ell^m, B_j Y_\ell^{m'} \rangle = 0$$

for every  $j = 1, 2, 3$ , and  $m, m' \in \{-\ell - 1, \dots, \ell + 1\}$ .

Moreover,

$$\langle Y_\ell^m, B_j Y_{\ell'}^{m'} \rangle = 0$$

with  $|\ell - \ell'| \geq 2$  for every  $m \in \{-\ell - 1, \dots, \ell + 1\}$ ,  $m' \in \{-\ell' - 1, \dots, \ell' + 1\}$ ,  $j = 1, 2, 3$ . In order to prove that the Lie–Galerkin Tracking Condition is satisfied, we choose a reordering  $(\phi_k)_{k \in \mathbb{N}}$  of the spherical harmonics in such a way that

$$\{\phi_k \mid k = 1, \dots, 4\ell + 4\} = \{Y_\ell^{-\ell}, \dots, Y_\ell^\ell, Y_{\ell+1}^{-\ell-1}, \dots, Y_{\ell+1}^{\ell+1}\},$$

and it remains to prove that

$$\text{Lie}\mathcal{V}_{4\ell+4} = \mathfrak{su}(4\ell + 4). \quad (11)$$

The characteristic spectral gap of the space

$$\mathcal{H}_\ell = \text{span}\{Y_\ell^{-\ell}, \dots, Y_\ell^\ell, Y_{\ell+1}^{-\ell-1}, \dots, Y_{\ell+1}^{\ell+1}\}$$

is  $(\ell + 1)(\ell + 2) - \ell(\ell + 1) = 2(\ell + 1)$ . In particular,  $(2(\ell + 1), 1)$ ,  $(2(\ell + 1), 2)$ , and  $(2(\ell + 1), 3)$  are in  $\Xi_{4\ell+4}$ .

The rest of Section 3 is devoted to showing that  $J_\xi(\mathcal{E}_{2\ell+1}(B_j^{(4\ell+4)}))$ , for  $\xi \in S^1$  and  $j = 1, 2, 3$ , generate  $\mathfrak{su}(4\ell + 4)$ , proving (11).

### 3.1. Matrix representations

Denote by  $\mathcal{J}_\ell$  the set of integer pairs  $\{(r, m) \mid r = \ell, \ell + 1, m = -r, \dots, r\}$ . Consider the lexicographic ordering  $\varrho : \{1, \dots, 4\ell + 4\} \rightarrow \mathcal{J}_\ell$ . For  $j, k = 1, \dots, 4\ell + 4$ , let  $e_{j,k}$  be the  $(4\ell + 4)$ -square matrix whose entries are all zero, except the one at row  $j$  and column  $k$ , which is equal to 1. Define

$$E_{j,k} = e_{j,k} - e_{k,j}, \quad F_{j,k} = ie_{j,k} + ie_{k,j}, \quad D_{j,k} = ie_{j,j} - ie_{k,k}.$$

By a slight abuse of notation, also set  $e_{\varrho(j), \varrho(k)} = e_{j,k}$ . The analogous identification can be used to define  $E_{\varrho(j), \varrho(k)}$ ,  $F_{\varrho(j), \varrho(k)}$ ,  $D_{\varrho(j), \varrho(k)}$ . Note that

$$J_i(E_{(\ell, m), (\ell+1, n)}) = -F_{(\ell, m), (\ell+1, n)} \quad \text{and} \quad J_i(F_{(\ell, m), (\ell+1, n)}) = E_{(\ell, m), (\ell+1, n)}.$$

Thanks to this notation, we can conveniently represent the matrices corresponding to the controlled vector field (projected onto  $\mathcal{H}_\ell$ ). A computation shows that

the control potentials in the  $x$  and  $y$  directions,  $B_1$  and  $B_2$  respectively, projected onto  $\mathcal{H}_\ell$ , have the matrix representations

$$B_1^{(4\ell+4)} = \sum_{m=-\ell}^{\ell} (-q_{\ell,m} F_{(\ell,m),(\ell+1,m-1)} + q_{\ell,-m} F_{(\ell,m),(\ell+1,m+1)}),$$

$$B_2^{(4\ell+4)} = \sum_{m=-\ell}^{\ell} (q_{\ell,m} E_{(\ell,m),(\ell+1,m-1)} + q_{\ell,-m} E_{(\ell,m),(\ell+1,m+1)}),$$

where

$$q_{\ell,m} = \sqrt{\frac{(\ell-m+2)(\ell-m+1)}{4(2\ell+1)(2\ell+3)}}.$$

Similarly, we associate with the control potential  $B_3$  in the  $z$  direction the matrix representation

$$B_3^{(4\ell+4)} = \sum_{m=-\ell}^{\ell} p_{\ell,m} F_{(\ell,m),(\ell+1,m)},$$

with

$$p_{\ell,m} = -\sqrt{\frac{(\ell+1)^2 - m^2}{(2\ell+1)(2\ell+3)}}.$$

### 3.2. Useful bracket relations

From the identity

$$[e_{j,k}, e_{n,m}] = \delta_{kn} e_{j,m} - \delta_{jm} e_{n,k}$$

we get the relations

$$[E_{j,k}, E_{k,n}] = E_{j,n}, \quad [F_{j,k}, F_{k,n}] = -E_{j,n}, \quad [E_{j,k}, F_{k,n}] = F_{j,n}, \quad (12)$$

and

$$[E_{j,k}, F_{j,k}] = 2D_{j,k}, \quad [F_{j,k}, D_{j,k}] = 2E_{j,k}. \quad (13)$$

The relations above can be interpreted following a “triangle rule”: the bracket between an operator coupling the states  $j$  and  $k$  and an operator coupling the states  $k$  and  $n$  couples the states  $j$  and  $n$ . On the other hand, the bracket is zero if two operators couple no common states, that is,

$$[Y_{j,k}, Z_{j',k'}] = 0 \quad \text{if } \{j, k\} \cap \{j', k'\} = \emptyset, \quad (14)$$

with  $Y, Z \in \{E, F, D\}$ .

### 3.3. Controllability in $\mathfrak{su}(4\ell + 4)$

**Lemma 3.2.** *The Lie algebra  $L$  generated by  $B_1^{(4\ell+4)}, B_2^{(4\ell+4)}, B_3^{(4\ell+4)}, J_i(B_1^{(4\ell+4)}), J_i(B_2^{(4\ell+4)}), J_i(B_3^{(4\ell+4)})$  is equal to  $\mathfrak{su}(4\ell + 4)$ .*

*Proof.* The first step of the proof consists in showing that the Lie algebra  $L$  contains the elementary matrices

$$E_{(\ell,k),(\ell+1,k+j)} \quad \text{for } k = -\ell, \dots, \ell, \quad j = -1, 0, 1. \quad (15)$$

With a slight abuse of notation and for the sake of readability, let us write  $B_j = B_j^{(4\ell+4)}$ ,  $j = 1, 2, 3$ . Let us also write  $\text{ad}_\alpha \beta$  for  $[\alpha, \beta]$  and  $\text{ad}_\alpha^{j+1} \beta$  for  $[\alpha, \text{ad}_\alpha^j \beta]$ .

Notice that

$$J_i(B_3) = \sum_{\ell=-m}^m p_{\ell,m} J_i(F_{(\ell,m),(\ell+1,m)}) = \sum_{\ell=-m}^m p_{\ell,m} E_{(\ell,m),(\ell+1,m)}.$$

By induction on  $j \geq 0$  and using the bracket relations (13), we have

$$\begin{aligned} \text{ad}_{B_3}^{2j} J_i(B_3) &= [B_3, [B_3, \text{ad}_{B_3}^{2j-2} J_i(B_3)]] \\ &= (-1)^j 2^{2j} \sum_{m=-\ell}^{\ell} p_{\ell,m}^{2j+1} E_{(\ell,m),(\ell+1,m)}. \end{aligned}$$

By invertibility of the Vandermonde matrix and since  $p_{\ell,m} \neq p_{\ell,n}$  for every  $n \neq m, -m$ , it follows that

$$E_{(\ell,-m),(\ell+1,-m)} + E_{(\ell,m),(\ell+1,m)} \in L, \quad \text{for } m = 0, \dots, \ell. \quad (16)$$

In particular,  $E_{(\ell,0),(\ell+1,0)} \in L$ . The double bracket of

$$\frac{B_2 - J_i(B_1)}{2} = \sum_{m=-\ell}^{\ell} q_{\ell,m} E_{(\ell,m),(\ell+1,m-1)} \in L \quad (17)$$

with  $E_{(\ell,0),(\ell+1,0)}$  is easily computed using (12) and (14) and gives

$$\begin{aligned} &\left[ \left[ \sum_{m=-\ell}^{\ell} q_{\ell,m} E_{(\ell,m),(\ell+1,m-1)}, E_{(\ell,0),(\ell+1,0)} \right], E_{(\ell,0),(\ell+1,0)} \right] = \\ &= -q_{\ell,1} [E_{(\ell,0),(\ell,1)}, E_{(\ell,0),(\ell+1,0)}] - q_{\ell,0} [E_{(\ell+1,-1),(\ell+1,0)}, E_{(\ell,0),(\ell+1,0)}] \\ &= q_{\ell,0} E_{(\ell,0),(\ell+1,-1)} + q_{\ell,1} E_{(\ell,1),(\ell+1,0)} \in L. \end{aligned}$$

Define

$$Q_m = \begin{cases} q_{\ell,0} E_{(\ell,0),(\ell+1,-1)} + q_{\ell,1} E_{(\ell,1),(\ell+1,0)} & \text{for } m = 0, \\ q_{\ell,-m} E_{(\ell,-m),(\ell+1,-m-1)} + q_{\ell,m+1} E_{(\ell,m+1),(\ell+1,m)} & \text{for } 0 < m < \ell, \\ q_{\ell,-\ell} E_{(\ell,-\ell),(\ell+1,-\ell-1)} & \text{for } m = \ell. \end{cases}$$

In particular,  $B_2 - J_i(B_1) = 2 \sum_{m=0}^{\ell} Q_m$ . Using again (12) and (14), we have

$$\left[ \left[ \sum_{m=k}^{\ell} Q_m, E_{(\ell,-k),(\ell+1,-k)} + E_{(\ell,k),(\ell+1,k)} \right], E_{(\ell,-k),(\ell+1,-k)} + E_{(\ell,k),(\ell+1,k)} \right] = Q_k,$$

for  $k = 1, \dots, \ell$ . By iteration on  $k$  and because of (16), it follows that  $Q_k \in L$  for  $k = 0, \dots, \ell$ .

Now, since  $Q_{\ell}/q_{\ell,-\ell} = E_{(\ell,-\ell),(\ell+1,-\ell-1)}$  is in  $L$ , then

$$\text{ad}_{E_{(\ell,-\ell),(\ell+1,-\ell-1)}}^2(E_{(\ell,-\ell),(\ell+1,-\ell)} + E_{(\ell,\ell),(\ell+1,\ell)}) = -E_{(\ell,-\ell),(\ell+1,-\ell)} \in L,$$

which, in turns, implies that

$$\text{ad}_{E_{(\ell,-\ell),(\ell+1,-\ell)}}^2(Q_{\ell-1}) = -q_{\ell,-\ell}E_{(\ell,-\ell+1),(\ell+1,-\ell)} \in L.$$

Iterating the argument,  $E_{(\ell,m),(\ell+1,m)}$  and  $E_{(\ell,m),(\ell+1,m-1)}$  are in  $L$  for every  $m = -\ell, \dots, \ell$ .

By the same argument as above with (17) replaced by

$$\frac{B_2 + J_i(B_1)}{2} = \sum_{m=-\ell}^{\ell} q_{\ell,-m}E_{(\ell,m),(\ell+1,m+1)} \in L,$$

we also have that  $E_{(\ell,m),(\ell+1,m+1)}$  is in  $L$  for every  $m = -\ell, \dots, \ell$ , proving (15). It then follows from (12) that each  $E_{j,k}$  is in  $L$ .

If we now replace (17) with

$$\frac{B_1 + J_i(B_2)}{2} = - \sum_{m=-\ell}^{\ell} q_{\ell,m}F_{(\ell,m),(\ell+1,m-1)} \in L,$$

or

$$\frac{B_1 - J_i(B_2)}{2} = \sum_{m=-\ell}^{\ell} q_{\ell,-m}F_{(\ell,m),(\ell+1,m+1)} \in L,$$

the arguments above prove that  $F_{(\ell,m),(\ell+1,m-1)}$  and  $F_{(\ell,m),(\ell+1,m+1)}$  are in  $L$  for every  $m = -\ell, \dots, \ell$ . The relations (12) and (13) then imply that  $L = \mathfrak{su}(4\ell + 4)$ .  $\square$

#### 4. Proof of Theorem 2.6

The outline of the proof is the following:

**Step 1.** Thanks to a change of coordinates in time and within  $\mathcal{H}$ , we restate the control problem in the so-called *interaction framework*, to handle the drift term in the Schrödinger operator. This is also useful to study, in Step 2, the controllability properties of the system via convexification techniques. (See Sections 4.1 and 4.2.)



**Step 2.** We develop the convexification procedure. We design the control law in order to excite a given spectral gap and set to zero all the elements of the control Hamiltonian corresponding to other spectral gaps. (See Sections 4.4 and 4.6.)

**Step 3.** The Lie–Galerkin Control Condition is used to prove that the dynamics obtained in Step 2 generate every unitary transformation of the finite dimensional Galerkin approximation. (See Section 4.5.)

**Step 4.** The sparsity structure of the dynamics obtained by convexification guarantees that the flows of the infinite-dimensional system and of the Galerkin approximations are as close as desired. (See Section 4.7.)

#### 4.1. Time-reparametrization

Up to replacing each  $B_j$  with  $\delta B_j$ , we can assume that  $\delta = 1$ .

For every piecewise constant function  $z$  such that  $z(t) \geq 1$  for every  $t$ , we consider the time-reparametrization

$$\frac{d\psi}{dt}(t) = (z(t)A + u_1(t)z(t)B_1 + \cdots + u_p(t)z(t)B_p)\psi(t) \quad (18)$$

of system (3). Each  $u_j(t)z(t)$  belongs to the time-varying set  $z(t)U_j$ .

If  $u_1, \dots, u_p$  are control laws in (18) then the corresponding controls in (3) are their time-reparametrizations  $\tilde{u}_j(s) = u_j(t(s))$  with  $t(s) = \int_0^s z(\tau)d\tau$ ,  $j = 1, \dots, p$ . By restricting the range of available controls and setting  $v_j(t) = u_j(t)z(t)$ , we can focus our attention on trajectories of

$$\frac{d\psi}{dt}(t) = (z(t)A + v_1(t)B_1 + \cdots + v_p(t)B_p)\psi(t), \quad (19)$$

with  $z(t) \geq 1$  and  $v(t) = (v_1(t), \dots, v_p(t)) \in U$ . Each solution of (19) with  $z$  and  $v$  piecewise constant is the time-reparametrization of a solution of (3) with piecewise constant controls (but the converse is not necessarily true, since we restricted the set of admissible controls). Hence, the approximate simultaneous controllability of (19) implies the approximate simultaneous controllability of (3). Moreover

$$\|\tilde{u}_j\|_{L^1} = \int_0^{t^{-1}(T)} |\tilde{u}_j(\tau)|d\tau = \int_0^T |u_j(t)|z(t)dt = \int_0^T |v_j(t)|dt \leq T,$$

for  $j = 1, \dots, p$ . The last inequality holds since either  $U_j = [0, 1]$  or  $U_j = [-1, 1]$ .

The  $L^1$ -bounded approximate simultaneous controllability of (3) is proved in the next sections by showing the approximate simultaneous controllability in  $\mathcal{L}$  of (19) with a bound on the controllability time which is uniform with respect to the tolerance.

#### 4.2. Interaction framework

Given a solution  $\psi(\cdot)$  of (19) with controls  $z(\cdot), v_1(\cdot), \dots, v_p(\cdot)$  and a piecewise constant function  $\alpha(\cdot)$  with values in  $\{0, 1\}$ , let us define

$$\omega(t) = \int_0^t (z(s) - \alpha(s)) ds$$

and

$$y(t) = e^{-\omega(t)A} \psi(t).$$

In particular

$$|\langle \phi_k, y(t) \rangle| = |\langle \phi_k, \psi(t) \rangle|, \quad k \in \mathbb{N}, \quad (20)$$

for every  $t$ . For  $\omega, v_1, \dots, v_p \in \mathbb{R}$  set  $\Theta(\omega, v_1, \dots, v_p) = e^{-\omega A} (v_1 B_1 + \dots + v_p B_p) e^{\omega A}$ . Note that

$$\begin{aligned} \Theta(\omega, v_1, \dots, v_p)_{jk} &= \langle \phi_k, \Theta(\omega, v_1, \dots, v_p) \phi_j \rangle \\ &= e^{i(\lambda_k - \lambda_j)\omega} (v_1 (B_1)_{jk} + \dots + v_p (B_p)_{jk}), \end{aligned} \quad (21)$$

and that  $y(\cdot)$  satisfies

$$\dot{y}(t) = (\alpha(t)A + \Theta(\omega(t), v_1(t), \dots, v_p(t)))y(t), \quad \alpha \in \{0, 1\}, \quad v \in U, \quad \dot{\omega} + \alpha \geq 1. \quad (22)$$

Conversely, each solution of (22) with  $\alpha \in \{0, 1\}$  and  $v \in U$  piecewise constant and  $\omega$  continuous and piecewise affine, with  $\dot{\omega} + \alpha = z \geq 1$  almost everywhere, is, up to a time-dependent change of coordinates preserving the modulus of each component with respect to the basis  $\Phi$ , a solution of (19) with  $u$  piecewise constant. In particular, each solution of

$$\dot{y}(t) = (\alpha(t)A + \Theta(\omega(t), v_1(t), \dots, v_p(t)))y(t), \quad \alpha \in \{0, 1\}, \quad v \in U, \quad \dot{\omega} \geq 1, \quad (23)$$

with  $\alpha, v$  piecewise constant and  $\omega$  continuous and piecewise affine is, up to a time-dependent change of coordinates preserving the modulus of each component, a solution of (19) with  $u$  piecewise constant (but the converse is not necessarily true).

**Proposition 4.1.** *Approximate simultaneous controllability of (23) implies approximate simultaneous controllability of (3). If, moreover, approximate simultaneous controllability in  $\mathcal{L} = \bigcup_{k \in \mathbb{N}} \text{span}\{\phi_1, \dots, \phi_k\}$  of (23) is achieved with a uniform bound on time then (3) is  $L^1$ -bounded approximately simultaneous controllable.*

*Proof.* The strategy of the proof follows [BCCS12, Proposition 6.1].

Approximate simultaneous controllability of (23) implies approximate simultaneous controllability of (19) in modulus thanks to (20).

Moreover, because of the unitarity of the evolution, the approximate simultaneous controllability of (23) is equivalent to the approximate simultaneous controllability of the system

$$\dot{y}(t) = -(\alpha(t)A + \Theta(\omega(t), v_1(t), \dots, v_p(t)))y(t), \quad \alpha \in \{0, 1\}, \quad v \in U, \quad \dot{\omega} \geq 1,$$

which implies approximate simultaneous controllability in modulus of the time-reversed version of (19).

Take  $r$  orthonormal initial conditions  $\psi_0^1, \dots, \psi_0^r$  and  $r$  orthonormal final conditions  $\psi_1^1, \dots, \psi_1^r$ . Since the spectrum of  $A$  is infinite by Assumption (A1) we can apply [BCCS12, Lemma 6.3] so that for every tolerance  $\eta > 0$  there exist  $k_1, \dots, k_r \in \mathbb{N}$  pairwise distinct such that

$$\mathcal{C} = \{e^{tA}\phi_{k_1} + \dots + e^{tA}\phi_{k_r} \mid t \in \mathbb{R}\}.$$

is  $\eta$ -dense in the torus

$$\mathcal{T} = \{e^{\theta_1 A}\phi_{k_1} + \dots + e^{\theta_r A}\phi_{k_r} \mid \theta_1, \dots, \theta_r \in \mathbb{R}\}.$$

By approximate simultaneous controllability in modulus of (19), it follows that there exists an admissible control  $(z, v)$  steering simultaneously each  $\psi_0^j$ , for  $j = 1, \dots, r$ ,  $\eta$ -close to  $e^{\theta_j A}\phi_{k_j}$  for some  $\theta_1, \dots, \theta_r \in \mathbb{R}$ .

Similarly, by approximate simultaneous controllability in modulus of the time-reversed equation of (19) there exists an admissible control  $(\tilde{z}, \tilde{v})$  steering system (19) simultaneously, for some  $\tilde{\theta}_1, \dots, \tilde{\theta}_r \in \mathbb{R}$ , from  $e^{\tilde{\theta}_1 A}\phi_{k_1}, \dots, e^{\tilde{\theta}_r A}\phi_{k_r}$  to an  $\eta$ -neighborhood of  $\psi_1^1, \dots, \psi_1^r$ .

The concatenation of the control  $(z, v)$ , of a control constantly equal to  $(1, 0)$  on a time interval of suitable length, and of  $(\tilde{z}, \tilde{v})$  steers system (19) simultaneously from  $\psi_0^1, \dots, \psi_0^r$  to a  $3\eta$ -neighborhood of  $\psi_1^1, \dots, \psi_1^r$ .

Finally, according to the conclusion of Section 4.1, the approximate simultaneous controllability of (19) implies approximate simultaneous controllability of (3).  $\square$

#### 4.3. Galerkin approximation

**Definition 4.2.** Let  $N \in \mathbb{N}$ . The *Galerkin approximation* of (23) of order  $N$  is the system

$$\dot{x} = (\alpha A^{(N)} + \Theta^{(N)}(\omega, v_1, \dots, v_p))x, \quad x \in \mathcal{H}, \quad (24)$$

where  $\Theta^{(N)}(\omega, v_1, \dots, v_p) = \pi_N \Theta(\omega, v_1, \dots, v_p) \pi_N$ . Recall that the elements of  $\Theta^{(N)}(\omega, v_1, \dots, v_p)$  are as in (21). The controls  $v$  are piecewise constant with values in  $U$ , while  $\omega$  is continuous and piecewise affine, with  $\dot{\omega} \geq 1$  almost everywhere.

In the following section we recall a convexification result whose role it is to identify the matrices that can be obtained by convexification of matrices of the form  $\Theta^{(N)}(\omega, v_1, \dots, v_p)$ .

#### 4.4. Convexification

The following technical result has been proved in [BCCS12, Lemma 4.3].

**Lemma 4.3.** Let  $\kappa$  be a positive integer and  $\gamma_1, \dots, \gamma_\kappa \in \mathbb{R} \setminus \{0\}$  be such that  $|\gamma_1| \neq |\gamma_j|$  for  $j = 2, \dots, \kappa$ . Let

$$\varphi(t) = (e^{it\gamma_1}, \dots, e^{it\gamma_\kappa}).$$

Then, for every  $\tau_0 \in \mathbb{R}$ , we have

$$\overline{\text{conv}\varphi([\tau_0, \infty))} \supseteq \varpi S^1 \times \{(0, \dots, 0)\},$$

where

$$\varpi = \prod_{k=2}^{\infty} \cos\left(\frac{\pi}{2k}\right) > 0. \quad (25)$$

Moreover, for every  $R > 0$  and  $\xi \in S^1$  there exists a sequence  $(\tau_k)_{k=1}^{\infty}$  such that  $\tau_1 \geq \tau_0$ ,  $\tau_{k+1} - \tau_k > R$ , and

$$\lim_{K \rightarrow \infty} \frac{1}{K} \sum_{k=1}^K \varphi(\tau_k) = (\varpi \xi, 0, \dots, 0).$$

#### 4.5. Control in $SU(n)$

Let  $n$  be such that hypothesis (5) holds true. Define the set of matrices

$$\begin{aligned} \mathcal{W}_n = & \left\{ A^{(n)} \right\} \cup \left\{ \mathcal{E}_0(B_j^{(n)}) \mid (0, j) \in \Xi_n \right\} \\ & \cup \left\{ \mathcal{E}_0(B_j^{(n)}) + \varpi \mathcal{E}_{\sigma}(B_j^{(n)}) \mid (\sigma, j) \in \Xi_n \right. \\ & \quad \left. \text{and } \sigma, j \text{ are such that } (0, j) \in \Xi_n, \sigma \neq 0 \right\} \\ & \cup \left\{ \varpi \mathcal{E}_{\sigma}(B_j^{(n)}) \mid (\sigma, j) \in \Xi_n, \sigma \neq 0, \text{ and } U_j = [-1, 1] \right\}, \end{aligned}$$

where  $\Xi_n$  and  $\varpi$  are defined as in (4) and (25), respectively. (Recall that by rescaling we are assuming  $\delta = 1$ .)

Notice that  $\text{Lie}(\mathcal{W}_n) = \text{Lie}(\mathcal{V}_n^0)$ .

Consider the auxiliary control system

$$\dot{x} = M(t)x, \quad M(t) \in \mathcal{W}_n, \quad (26)$$

where  $M$  plays the role of control. It follows from (5) and standard controllability results on compact Lie groups (see [JS72]) that for every  $g \in SU(n)$  there exists a piecewise constant function  $M : [0, T] \rightarrow \mathcal{W}_n$  such that

$$\overrightarrow{\exp} \int_0^T M(s) ds = g,$$

where the chronological notation  $\overrightarrow{\exp} \int_0^t V_s ds$  is used for the flow from time 0 to time  $t$  of the time-varying equation  $\dot{q} = V_s(q)$ ,  $q \in \mathbb{C}^n$  (see [AS04]).

We stress that  $T$  can be bounded from above by a constant depending on  $n$  and  $\mathcal{W}_n$  but not on  $g$ .

#### 4.6. System reduction by convexification

Let  $n$  be fixed as in the previous section. For every  $N \geq n$  let

$$\begin{aligned} \mathcal{W}_{n,N} = & \left\{ A^{(N)} \right\} \cup \left\{ \mathcal{E}_0(B_j^{(N)}) \mid (0, j) \in \Xi_n \right\} \\ & \cup \left\{ \mathcal{E}_0(B_j^{(N)}) + \mathfrak{w}\mathcal{E}_\sigma(B_j^{(N)}) \mid (\sigma, j) \in \Xi_n \right. \\ & \quad \left. \text{and } \sigma, j \text{ are such that } (0, j) \in \Xi_n, \sigma \neq 0 \right\} \\ & \cup \left\{ \mathfrak{w}\mathcal{E}_\sigma(B_j^{(N)}) \mid (\sigma, j) \in \Xi_n, \sigma \neq 0, \text{ and } U_j = [-1, 1] \right\}. \end{aligned}$$

**Lemma 4.4.** *For every  $N \geq n$  and for every piecewise constant  $M : [0, T] \rightarrow \mathcal{W}_{n,N}$  there exist  $\alpha : [0, T] \rightarrow \{0, 1\}$ ,  $v : [0, T] \rightarrow U$  piecewise constant and a sequence  $(\omega_h(\cdot))_{h \in \mathbb{N}}$  of continuous and piecewise affine functions from  $[0, T]$  to  $[0, \infty)$  with  $\dot{\omega}_h \geq 1$  almost everywhere, such that*

$$\left\| \int_0^t (\alpha(s)A^{(N)} + \Theta^{(N)}(\omega_h(s), v_1(s), \dots, v_p(s)))ds - \int_0^t M(s)ds \right\| \rightarrow 0$$

uniformly with respect to  $t \in [0, T]$  as  $h$  tends to infinity.

*Proof.* Let  $N \geq n$ . Define  $\alpha(t)$  and  $v_1(t), \dots, v_p(t)$  at each  $t \in [0, T]$  as follows: if  $M(t) = A^{(N)}$  then  $\alpha(t) = 1$  and  $v_1(t) = \dots = v_p(t) = 0$ ; otherwise, if  $M(t) = \mathcal{E}_0(B_j^{(N)})$ ,  $M(t) = \mathcal{E}_0(B_j^{(N)}) + \mathfrak{w}\mathcal{E}_\sigma(B_j^{(N)})$ , or  $M(t) = \mathfrak{w}\mathcal{E}_\sigma(B_j^{(N)})$  for some  $j$ , then take such a  $j$  minimal and set  $v_j(t) = 1$  and  $\alpha(t) = v_k(t) = 0$  for  $k \neq j$ .

We are going to apply Lemma 4.3 for every interval on which  $M(\cdot)$  is constant. Fix  $\omega_h(0) = 0$  for every  $h$ . Take an interval  $(t_0, t_1)$  on which  $M(\cdot)$  is constant and assume that  $\omega_h(t_0)$  has been computed. We next extend  $\omega_h$  on  $(t_0, t_1)$ .

If  $\alpha = 1$  on  $(t_0, t_1)$  then take  $\omega_h(\tau) = \omega_h(t_0) + \tau - t_0$  for every  $\tau \in (t_0, t_1)$ .

Otherwise, let  $v_j = 1$  on  $(t_0, t_1)$  and assume for now that  $M(t) = \mathcal{E}_0(B_j^{(N)}) + \mathfrak{w}\mathcal{E}_\sigma(B_j^{(N)})$ . Apply Lemma 4.3 with  $\gamma_1 = \sigma$ ,  $\{\gamma_2, \dots, \gamma_\kappa\} = \Sigma_N \setminus \{\sigma\}$ ,  $\xi = 1$ ,  $R = T$ , and  $\tau_0 = \omega_h(t_0)$ . Then there exists a sequence  $(\tau_k)_{k=1}^\infty$  such that  $\tau_1 \geq \omega_h(t_0)$ ,  $\tau_{k+1} - \tau_k > T$ , and

$$\lim_{K \rightarrow \infty} \frac{1}{K} \sum_{k=1}^K (e^{i\tau_k \gamma_1}, \dots, e^{i\tau_k \gamma_\kappa}) = (\mathfrak{w}, 0, \dots, 0).$$

In particular there exists  $K = K(h)$  such that

$$\left| \frac{1}{K} \sum_{k=1}^K e^{i(\lambda_l - \lambda_m)\tau_k} b_{ml}^{(j)} - \left( \mathcal{E}_0(B_j^{(N)}) + \mathfrak{w}\mathcal{E}_\sigma(B_j^{(N)}) \right)_{m,l} \right| < \frac{1}{h},$$

for every  $1 \leq l, m \leq N$ .

Consider the piecewise constant function  $Y : (t_0, t_1) \rightarrow \mathbb{R}$  defined as follows: set

$$s_\alpha = t_1 + (t_1 - t_0) \frac{\alpha}{K}, \quad \alpha = 0, \dots, K,$$

and let

$$Y(t) = \omega_h(t_0) + \sum_{\alpha=1}^K \tau_\alpha \chi_{[s_{\alpha-1}, s_\alpha)}(t), \quad t \in (t_0, t_1).$$

By a simple smoothing procedure (see for instance [BCCS12, Proposition 5.5]) one can construct a continuous piecewise affine approximation  $\omega_h : [t_0, t_1] \rightarrow \mathbb{R}$  of  $Y$  with  $\dot{\omega}_h \geq 1$  almost everywhere such that

$$\left\| \int_{t_0}^t (\Theta^{(N)}(\omega_h(s), v_1(s), \dots, v_p(s))) ds - \int_{t_0}^t M(s) ds \right\| \rightarrow 0 \quad (27)$$

uniformly with respect to  $t \in [t_0, t_1]$  as  $h$  tends to infinity.

The same argument can be carried out in the case in which  $M(t) = \mathcal{E}_0(B_j^{(N)})$  by applying Lemma 4.3 with  $\gamma_1$  in  $(0, \infty) \setminus \Sigma_N$ ,  $\{\gamma_2, \dots, \gamma_\kappa\} = \Sigma_N$ ,  $\xi = 1$ ,  $R = T$ , and  $\tau_0 = \omega_h(t_0)$ .

The final case to be considered is when  $M(t) = \varpi \mathcal{E}_\sigma(B_j^{(N)})$  with  $\sigma \neq 0$ ,  $(\sigma, j) \in \Xi_n$ , and  $U_j = [-1, 1]$ . Notice that

$$\varpi \mathcal{E}_\sigma(B_j^{(N)}) = \frac{(\mathcal{E}_0(B_j^{(N)}) + \varpi \mathcal{E}_\sigma(B_j^{(N)})) - (\mathcal{E}_0(B_j^{(N)}) + \varpi J_{-1}(\mathcal{E}_\sigma(B_j^{(N)})))}{2}. \quad (28)$$

The argument above can be easily adapted to matrices  $M(t)$  of the type  $v_j(\mathcal{E}_0(B_j^{(N)}) + \varpi J_\xi(\mathcal{E}_\sigma(B_j^{(N)})))$ , with  $v_j \in U_j$ ,  $\xi \in S^1$  (not assuming  $\xi = 1$  when applying Lemma 4.3), and in particular to  $-(\mathcal{E}_0(B_j^{(N)}) + \varpi J_{-1}(\mathcal{E}_\sigma(B_j^{(N)})))$ .

It suffices then to introduce a sequence  $(M^h)_{h \in \mathbb{N}}$  of piecewise constant functions with values in

$$\{v_j(\mathcal{E}_0(B_j^{(N)}) + \varpi J_\xi(\mathcal{E}_\sigma(B_j^{(N)}))) \mid v_j \in U_j, \xi \in S^1\}$$

such that  $\int_{t_0}^t M^h(s) ds$  converges uniformly for  $t \in [t_0, t_1]$  to  $\int_{t_0}^t M(s) ds$  as  $h$  tends to infinity and to apply a diagonal procedure based on the approximation introduced above.  $\square$

As a consequence of the lemma above and thanks to [AS04, Lemma 8.2], we have

$$\left\| \overrightarrow{\exp} \int_0^t \left( \alpha(s) A^{(N)} + \Theta^{(N)}(\omega_h(s), v_1(s), \dots, v_p(s)) \right) ds - \overrightarrow{\exp} \int_0^t M(s) ds \right\| \rightarrow 0 \quad (29)$$

uniformly with respect to  $t \in [0, T]$  as  $h$  tends to infinity.

#### 4.7. Control of the infinite-dimensional system

Proposition 4.5 below states that we can pass to the limit in (29) as  $N$  tends to infinity. Its proof is based on the sparsity structure of the matrices in  $\mathcal{W}_{n,N}$ , guaranteeing that the dynamics of the infinite-dimensional system and the one of the Galerkin approximations are as close as desired.

We introduce the following notation: given  $n \in \mathbb{N}$  and a bounded linear transformation  $L$  of  $\mathcal{H}$ , let  $\text{Crop}_n(L)$  be the  $n \times n$  matrix  $(\langle \phi_j, L\phi_k \rangle)_{j,k=1}^n$ . We use the same symbol  $\text{Crop}_n$  also to denote the similar cropping operation acting on the space of  $N \times N$  matrices, with  $N \geq n$ .

**Proposition 4.5.** *Let  $n \in \mathbb{N}$  and  $M : [0, T] \rightarrow \mathcal{W}_n$  be piecewise constant. Then, for every  $\varepsilon > 0$ , there exist piecewise constant controls  $z : [0, T] \rightarrow [1, \infty)$  and  $v : [0, T] \rightarrow U$ , and a continuous piecewise affine function  $\omega$  with  $\dot{\omega} \geq 1$  such that the propagator  $\Psi$  of (23) satisfies*

$$\left\| \overrightarrow{\exp} \int_0^t M(s) ds - \text{Crop}_n(\Psi_t) \right\| < \varepsilon,$$

for every  $t \in [0, T]$ .

*Proof.* Consider  $\mu > 0$  to be fixed later. For every  $j \in \mathbb{N}$  the hypothesis that  $\phi_j$  belongs to  $D(B_l)$  implies that the sequence  $((B_l)_{jk})_{k \in \mathbb{N}}$  is in  $\ell^2$  for every  $l = 1, \dots, p$ . It is therefore possible to choose  $N \geq n$  in such a way that  $\|((B_l)_{jk})_{k > N}\|_{\ell^2} < \mu$  for every  $j = 1, \dots, n$  and  $l = 1, \dots, p$ .

Let  $\hat{M}$  be a piecewise constant function from  $[0, T]$  to  $\mathcal{W}_{n,N}$  such that  $\text{Crop}_n \hat{M}(t) = M(t)$  for every  $t$  in  $[0, T]$ . Because of the definition of  $\Xi_n$  and of the classes  $\mathcal{W}_{n,N}$  and  $\mathcal{W}_n$  we have

$$\overrightarrow{\exp} \int_s^t \hat{M}(\tau) d\tau = \left( \begin{array}{c|c} \overrightarrow{\exp} \int_s^t M(\tau) d\tau & 0 \\ \hline 0 & * \end{array} \right).$$

By Lemma 4.4, for every  $\eta > 0$ , there exist piecewise constant controls  $\alpha : [0, T] \rightarrow \{0, 1\}$ ,  $v : [0, T] \rightarrow U$  and a continuous piecewise affine function  $\omega$  with  $\dot{\omega} \geq 1$  such that

$$\left\| \overrightarrow{\exp} \int_s^t \left( \alpha(\tau) A^{(N)} + \Theta^{(N)}(\omega(\tau), v_1(\tau), \dots, v_p(\tau)) \right) d\tau - \overrightarrow{\exp} \int_s^t \hat{M}(\tau) d\tau \right\| < \eta,$$

for every  $s, t$  in  $[0, T]$ .

Consider the solution  $\Psi$  of (23) associated with  $\alpha$ ,  $\omega$  and  $v$ . Set, for  $k \in \mathbb{N}$ ,

$$Q_t^{(k)} = \text{Crop}_k \Psi_t.$$

Now

$$\dot{Q}_t^{(N)} = \left( \alpha A^{(N)} + \Theta^{(N)}(\omega, v_1, \dots, v_p) \right) Q_t^{(N)} + R_t^{(N)},$$

and the choice of  $N$  is such that

$$|(R_t^{(N)})_{j,k}| \leq \mu, \quad (30)$$

for every  $j = 1, \dots, n$  and  $k = 1, \dots, N$ . Notice, moreover, that the norm of  $R_t^{(N)}$  can be uniformly bounded by a positive constant  $C$  independent of  $\eta$  (possibly depending on  $N$  and hence on  $\mu$ ).

By the variation formula and since  $Q_t^{(n)} = \text{Crop}_n(Q_t^{(N)})$  we have

$$Q_t^{(n)} = \text{Crop}_n \left[ \overrightarrow{\exp} \int_0^t \left( \alpha(\tau) A^{(N)} + \Theta^{(N)}(\omega(\tau), v_1(\tau), \dots, v_p(\tau)) \right) d\tau + \int_0^t \left( \overrightarrow{\exp} \int_s^t \left( \alpha(\tau) A^{(N)} + \Theta^{(N)}(\omega(\tau), v_1(\tau), \dots, v_p(\tau)) \right) d\tau \right) R_s^{(N)} ds \right],$$

so that

$$\begin{aligned} & \left\| \text{Crop}_n \left( \Psi_t - \overrightarrow{\exp} \int_0^t \left( \alpha(\tau) A^{(N)} + \Theta^{(N)}(\omega(\tau), v_1(\tau), \dots, v_p(\tau)) \right) d\tau \right) \right\| \\ & \leq t\eta C + \left\| \int_0^t \left( \overrightarrow{\exp} \int_s^t M(\tau) d\tau \right) \text{Crop}_n \left( R_s^{(N)} \right) ds \right\|. \end{aligned}$$

The norm of the matrix product

$$\left( \overrightarrow{\exp} \int_s^t M(\tau) d\tau \right) \text{Crop}_n \left( R_s^{(N)} \right)$$

is equal to

$$\| \text{Crop}_n R_s^{(N)} \|.$$

The *max* norm of  $\text{Crop}_n R_s^{(N)}$  is smaller than  $\mu$  by (30). Hence

$$\begin{aligned} & \left\| \text{Crop}_n \left( \Psi_t - \overrightarrow{\exp} \int_0^t \left( \alpha(\tau) A^{(N)} + \Theta^{(N)}(\omega(\tau), v_1(\tau), \dots, v_p(\tau)) \right) d\tau \right) \right\| \\ & \leq T(\eta C + \sqrt{n}\mu). \end{aligned}$$

The constant  $T(\eta C + \sqrt{n}\mu)$  can be made arbitrarily small by choosing  $\mu$  small with respect to  $n$  and  $T$  and then  $\eta$  small with respect to  $C = C(\mu)$  and  $T$ .  $\square$

Based on the previous results, we can now easily complete the proof of Theorem 2.6.

*Proof of Theorem 2.6.* Let  $r$  in  $\mathbb{N}$ ,  $\psi_1, \dots, \psi_r$  in  $\mathcal{H}$ ,  $\hat{\Upsilon}$  in  $\mathbf{U}(\mathcal{H})$ , and  $\varepsilon > 0$ . Let  $n_0$  be large enough so that there exists  $g \in SU(n_0)$  for which

$$|\langle \phi_j, \hat{\Upsilon} \psi_k \rangle - \langle \pi_{n_0} \phi_j, g \pi_{n_0} \psi_k \rangle| < \varepsilon,$$

for every  $1 \leq k \leq r$  and  $j \in \mathbb{N}$ .



Let  $n \geq n_0$  be such that hypothesis (5) is satisfied. Notice that if  $\psi_1, \dots, \psi_r$  and  $\hat{\Upsilon}(\psi_1), \dots, \hat{\Upsilon}(\psi_r)$  are in  $\mathcal{L}$  then  $n$  can be taken independently of  $\varepsilon$ .

From Section 4.5, there exists  $M : [0, T] \rightarrow \mathcal{W}_n$  such that

$$\overrightarrow{\exp} \int_0^T M(s) ds = g,$$

where  $g$  is seen as an element of  $SU(n)$ .

Proposition 4.5 ensures the existence of two piecewise constant functions  $z$  and  $v$  and of a continuous piecewise affine function  $\omega$  with  $\dot{\omega} \geq 1$  almost everywhere such that the associated propagator  $\Psi$  of (23) satisfies

$$\left\| \overrightarrow{\exp} \int_0^T M(s) ds - \text{Crop}_n(\Psi_T) \right\| < \varepsilon.$$

If  $\psi_1, \dots, \psi_r, \hat{\Upsilon}(\psi_1), \dots, \hat{\Upsilon}(\psi_r)$  are in  $\mathcal{L}$  then  $T$  is independent of  $\varepsilon$ . By Proposition 4.1 system (3) is  $L^1$ -bounded approximately simultaneously controllable.  $\square$

## 5. Proof of Theorem 2.8

The proof of Theorem 2.8 follows the same scheme as the one of Theorem 2.6. The key new argument is the following: it has been proved in Proposition 4.5 that system (19) can track every trajectory of (26). The idea is to replace (26) with a system which can track with arbitrary precision every trajectory in  $SU(n)$ . The crucial property, beyond the Lie bracket generating condition, that the new version of (26) should satisfy in order to achieve this goal is to be driftless (i.e., the time-reversal of each admissible trajectory is itself admissible).

The same time-reparameterization and time-dependent change of coordinates as in Section 4.1 allows one to consider the tracking problem for system (23) instead of system (3). As in the previous section we consider  $\delta$  to be renormalized to 1.

We can then base our argument on the following analogue of Proposition 4.1.

**Proposition 5.1.** *If (23) is a  $m$ -tracker then (3) is a  $m$ -tracker as well.*

The following proposition allows one to reduce a tracking problem in the space of unitary operators of  $\mathcal{H}$  to a tracking problem in  $SU(n)$  for  $n$  large enough. Its proof can be found in [BCCS12, Proposition 5.7].

**Proposition 5.2.** *Let  $\hat{\Upsilon} : [0, T] \rightarrow \mathbf{U}(\mathcal{H})$  be a continuous curve. Take  $\varepsilon > 0$  and  $m \in \mathbb{N}$ . Then for  $n \geq m$  sufficiently large there exists a continuous curve  $g : [0, T] \rightarrow SU(n)$  such that  $|\langle \phi_j, \hat{\Upsilon}(t)\phi_k \rangle - \langle e_j, g(t)e_k \rangle| < \varepsilon$  for every  $t$  in  $[0, T]$ ,  $1 \leq k \leq m$ , and  $j = 1, \dots, n$ , where  $(e_1, \dots, e_n)$  denotes the canonical basis of  $\mathbb{R}^n$ .*

Let  $n$  be chosen as in Proposition 5.2. According to the Lie–Galerkin Tracking Condition, we can assume, without loss of generality, that  $\text{Lie}(\mathcal{V}_n) = \mathfrak{su}(n)$ .

The roles played in Sections 4.5 and 4.6 by  $\mathcal{W}_n$  and  $\mathcal{W}_{n,N}$  are now played by  $\mathfrak{w}\mathcal{V}_n$  and  $\mathfrak{w}\mathcal{V}_{n,N}$ , where  $\mathcal{V}_n$  is defined as in (6) and

$$\mathcal{V}_{n,N} = \left\{ J_\xi(\mathcal{E}_\sigma(B_j^{(N)})) \mid (\sigma, j) \in \Xi_n, \sigma \neq 0, \xi \in S^1 \right\}.$$

In particular, we consider the auxiliary control system

$$\dot{x} = M(t)x, \quad M(t) \in \mathfrak{w}\mathcal{V}_n, \quad (31)$$

with  $M$  being the matrix-valued control parameter. It follows from the equality  $\text{Lie}(\mathcal{V}_n) = \mathfrak{su}(n)$  and Rashevski–Chow’s theorem that every trajectory on  $SU(n)$  can be tracked with arbitrary precision (up to time-reparameterization) by a trajectory of (31).

The relation between the trajectories of (24) and those of (31) (or, more precisely,  $\dot{x} = M(t)x$ ,  $M(t) \in \mathfrak{w}\mathcal{V}_{n,N}$ ), is described by the following lemma.

**Lemma 5.3.** *For every  $N \geq n$  and for every piecewise constant  $M : [0, T] \rightarrow \mathfrak{w}\mathcal{V}_{n,N}$  there exist  $\alpha : [0, T] \rightarrow \{0, 1\}$ ,  $v : [0, T] \rightarrow U$  piecewise constant, and a sequence  $(\omega_h(\cdot))_{h \in \mathbb{N}}$  of continuous and piecewise affine functions from  $[0, T]$  to  $[0, \infty)$  with  $\dot{\omega}_h \geq 1$  almost everywhere such that*

$$\left\| \int_0^t \left( \alpha(s)A^{(N)} + \Theta^{(N)}(\omega_h(s), v_1(s), \dots, v_p(s)) \right) ds - \int_0^t M(s)ds \right\| \rightarrow 0$$

uniformly with respect to  $t \in [0, T]$  as  $h$  tends to infinity.

*Proof.* The proof is almost identical to that of Lemma 4.4 in the case  $M(t) = \mathfrak{w}\mathcal{E}_\sigma(B_j^{(N)})$ . The only difference is in replacing (28) with

$$\mathfrak{w}J_\xi(\mathcal{E}_\sigma(B_j^{(N)})) = \frac{(\mathcal{E}_0(B_j^{(N)}) + \mathfrak{w}J_\xi(\mathcal{E}_\sigma(B_j^{(N)}))) - (\mathcal{E}_0(B_j^{(N)}) + \mathfrak{w}J_{-\xi}(\mathcal{E}_\sigma(B_j^{(N)})))}{2}.$$

We then apply the same convexification argument.  $\square$

As in the previous section, the lemma above and [AS04, Lemma 8.2] imply that

$$\begin{aligned} & \left\| \overrightarrow{\exp} \int_0^t \left( \alpha(s)A^{(N)} + \Theta^{(N)}(\omega_h(s), v_1(s), \dots, v_p(s)) \right) ds \right. \\ & \quad \left. - \overrightarrow{\exp} \int_0^t M(s)ds \right\| \rightarrow 0 \end{aligned} \quad (32)$$

uniformly with respect to  $t \in [0, T]$  as  $h$  tends to infinity.

In analogy with Section 4.7 we can conclude the proof of Theorem 2.8 thanks to the proposition below, which states that we can pass to the limit in (32) as  $N$  tends to infinity. Its proof is basically the same as the one of Proposition 4.5.

**Proposition 5.4.** *Let  $n \in \mathbb{N}$  and  $M : [0, T] \rightarrow \mathfrak{W}\mathcal{V}_n$  be piecewise constant. Then, for every  $\varepsilon > 0$ , there exist piecewise constant controls  $z : [0, T] \rightarrow [1, \infty)$  and  $v : [0, T] \rightarrow U$ , and a continuous piecewise affine function  $\omega$  with  $\dot{\omega} \geq 1$  almost everywhere such that the propagator  $\Psi$  of (23) satisfies*

$$\left\| \overrightarrow{\exp} \int_0^t M(s) ds - \text{Crop}_n(\Psi_t) \right\| < \varepsilon,$$

for every  $t \in [0, T]$ .

**Remark 5.5.** The hypothesis that each  $U_j$  contains 0 in its interior can be relaxed. Indeed, up to reordering, let  $p'$  be such that  $U_j = [0, \delta]$  if  $j = 1, \dots, p'$  and  $U_j = [-\delta, \delta]$  for  $j > p'$ . Assume that, for every  $j \in \{1, \dots, p'\}$ , if  $l \neq k$  are such that  $\lambda_l = \lambda_k$ , then  $\langle \phi_l, B_j \phi_k \rangle = 0$ . Assume, moreover, that the Lie–Galerkin Control Condition is satisfied with  $\mathcal{V}_n$  replaced by the set of all matrices  $J_\xi(\mathcal{E}_\sigma(B_j^{(n)}))$  with  $(\sigma, j) \in \Xi_n$ ,  $\xi \in S^1$ ,  $\sigma \neq 0$ , and either  $j > p'$  or the following holds: if  $l, k, l', k' \in \{1, \dots, n\}$  satisfy  $\lambda_l - \lambda_k = \lambda_{l'} - \lambda_{k'} = \sigma$  and

$$\langle \phi_l, B_j \phi_k \rangle \neq 0 \neq \langle \phi_{l'}, B_j \phi_{k'} \rangle,$$

then

$$\langle \phi_l, B_j \phi_l \rangle - \langle \phi_k, B_j \phi_k \rangle = \langle \phi_{l'}, B_j \phi_{l'} \rangle - \langle \phi_{k'}, B_j \phi_{k'} \rangle.$$

In this case the proof of Lemma 5.3 becomes more technically involved. The point is that, even if  $\mathcal{E}_0(B_j^{(N)})$  cannot be eliminated by convexification, it is a diagonal matrix by hypothesis. Hence, it can be used to define a new interaction framework. The sequence  $(\omega_h(\cdot))_h$  can then be constructed following [BCCS12, Proposition 5.5].

## 6. Proof of Theorem 2.12

First, let us prove  $L^1$ -bounded approximate simultaneous controllability for system (3) in  $s/2$ -norm for initial and final data in  $\mathcal{L}$ . Namely, we want to prove that, for  $r \in \mathbb{N}$ ,  $\psi_1, \dots, \psi_r \in \mathcal{L}$ , and  $\hat{\Upsilon} \in \mathbf{U}(\mathcal{H})$  with  $\hat{\Upsilon}\psi_1, \dots, \hat{\Upsilon}\psi_r \in \mathcal{L}$ , there exists  $K > 0$  such that the following holds: For every  $\varepsilon > 0$  there exists a control  $u$ , with  $\|u\|_{L^1} \leq K$ , such that

$$\|\psi_j - \Upsilon_T^u \psi_j\|_{s/2} < \varepsilon, \quad j = 1, \dots, r. \quad (33)$$

Let  $N$  be such that  $\psi_1, \dots, \psi_r$  and  $\hat{\Upsilon}\psi_1, \dots, \hat{\Upsilon}\psi_r$  are in  $\text{span}\{\phi_1, \dots, \phi_N\}$ . Note that on  $\text{span}\{\phi_1, \dots, \phi_N\}$  we have

$$\|\psi\|_{s/2} = \left( \sum_{k=1}^N |\lambda_k|^s |\langle \phi_k, \psi \rangle|^2 \right)^{1/2} \leq (\max\{|\lambda_1|, |\lambda_N|\})^{s/2} \|\psi\|. \quad (34)$$

Since system (3) is  $L^1$ -bounded approximately simultaneously controllable, there exists  $K > 0$  such that for every  $\varepsilon > 0$  there exists a piecewise constant control  $u$  with  $\|u\|_{L^1} \leq K$  and

$$\|\psi_j - \Upsilon_T^u \psi_j\| < \varepsilon, \quad j = 1, \dots, r.$$

Hence (34) implies  $L^1$ -bounded approximate simultaneous controllability in  $s/2$ -norm in  $\mathcal{L}$ .

Now let  $\psi_1, \dots, \psi_r \in D(|A|^{s/2})$  and  $\hat{\Upsilon} \in \mathbf{U}(\mathcal{H})$  be such that  $\hat{\Upsilon}\psi_1, \dots, \hat{\Upsilon}\psi_r \in D(|A|^{s/2})$ . Let  $\varepsilon > 0$  and consider  $\psi_1^0, \dots, \psi_r^0$  and  $\psi_1^1, \dots, \psi_r^1$  in  $\mathcal{L}$  such that

$$\|\psi_j^0 - \psi_j\|_{s/2} < \varepsilon \quad \text{and} \quad \|\psi_j^1 - \hat{\Upsilon}\psi_j\|_{s/2} < \varepsilon,$$

for  $j = 1, \dots, r$ . As proved above (see (33)), there exist  $K$ , independent on  $\varepsilon$ , and a piecewise constant control  $u$  with  $\|u\|_{L^1} \leq K$  such that

$$\|\psi_j^1 - \Upsilon_T^u \psi_j^0\|_{s/2} < \varepsilon, \quad j = 1, \dots, r.$$

By [BCC13, Proposition 2] and since system (3) is  $s$ -weakly coupled, there exists a constant  $C$  depending only on  $s$  and  $A, B_1, \dots, B_p$  such that

$$\|\Upsilon_T^u \psi\|_{s/2} \leq C^K \|\psi\|_{s/2},$$

for every  $\psi \in D(|A|^{s/2})$ . Therefore

$$\begin{aligned} \|\Upsilon_T^u(\psi_j) - \hat{\Upsilon}(\psi_j)\|_{s/2} &\leq \|\Upsilon_T^u(\psi_j - \psi_j^0)\|_{s/2} + \|\Upsilon_T^u \psi_j^0 - \psi_j^1\|_{s/2} + \|\psi_j^1 - \hat{\Upsilon}\psi_j\|_{s/2} \\ &\leq (C^K + 2)\varepsilon, \end{aligned}$$

for  $j = 1, \dots, r$ . □

**Remark 6.1.** Using arguments similar to those of the proof of Theorems 2.6 and 2.12, it is possible to prove a finer statement than Corollary 2.13. Indeed it is possible to prove that a system that satisfies Assumptions (A'), the Lie–Galerkin Tracking Condition, and is  $s$ -weakly coupled is an m-tracker for the  $s/2$ -norm. This is due to the fact that the Lie–Galerkin Tracking Condition actually implies m-tracking in  $\mathcal{L}$  with a uniform bound on the  $L^1$  norm of the control.

[AB05] Riccardo Adami and Ugo Boscain. Controllability of the Schrödinger equation via intersection of eigenvalues. In *Proceedings of the 44th IEEE Conference on Decision and Control*, pages 1080–1085, 2005.

[AS04] Andrei A. Agrachev and Yuri L. Sachkov. *Control theory from the geometric viewpoint*, volume 87 of *Encyclopaedia of Mathematical Sciences*. Springer-Verlag, Berlin, 2004. Control Theory and Optimization, II.

[BBR10] Anthony M. Bloch, Roger W. Brockett, and Chitra Rangan. Finite controllability of infinite-dimensional quantum systems. *IEEE Trans. Automat. Control*, 55(8):1797–1805, 2010.

[BC06] Karine Beauchard and Jean-Michel Coron. Controllability of a quantum particle in a moving potential well. *J. Funct. Anal.*, 232(2):328–389, 2006.

- [BCC13] N. Boussaïd, M. Caponigro, and T. Chambrion. Weakly-coupled systems in quantum control. *IEEE Trans. Automat. Control*, 58(9):2205–2216, 2013.
- [BCCS12] U. Boscain, M. Caponigro, T. Chambrion, and M. Sigalotti. A weak spectral condition for the controllability of the bilinear Schrödinger equation with application to the control of a rotating planar molecule. *Comm. Math. Phys.*, 311(2):423–455, 2012.
- [BCG<sup>+</sup>02] Ugo Boscain, Grégoire Charlot, Jean-Paul Gauthier, Stéphane Guérin, and Hans-Rudolf Jauslin. Optimal control in laser-induced population transfer for two- and three-level quantum systems. *J. Math. Phys.*, 43(5):2107–2132, 2002.
- [BCM<sup>+</sup>09] Ugo Boscain, Thomas Chambrion, Paolo Mason, Mario Sigalotti, and Dominique Sugny. Controllability of the rotation of a quantum planar molecule. In *Proceedings of the 48th IEEE Conference on Decision and Control*, pages 369–374, 2009.
- [BCMS12] Ugo Boscain, Francesca Chittaro, Paolo Mason, and Mario Sigalotti. Adiabatic control of the Schroedinger equation via conical intersections of the eigenvalues. *IEEE Trans. Automat. Control*, 57(8):1970–1983, 2012.
- [BL10] Karine Beauchard and Camille Laurent. Local controllability of 1D linear and nonlinear Schrödinger equations with bilinear control. *J. Math. Pures Appl.*, 94(5):520–554, 2010.
- [BMS82] J. M. Ball, J. E. Marsden, and M. Slemrod. Controllability for distributed bilinear systems. *SIAM J. Control Optim.*, 20(4):575–597, 1982.
- [BN10] Karine Beauchard and Vahagn Nersesyan. Semi-global weak stabilization of bilinear Schrödinger equations. *C. R. Math. Acad. Sci. Paris*, 348(19-20):1073–1078, 2010.
- [Bro72] R. W. Brockett. System theory on group manifolds and coset spaces. *SIAM J. Control*, 10:265–284, 1972.
- [CBCS11] M. Caponigro, U. Boscain, T. Chambrion, and M. Sigalotti. Q-track. Software registered at “Agence pour la Protection des Programmes” IDDN.FR.001.110021.000.S.P.2011.000.10000, 2011.
- [CH90] C. E. Carroll and F. T. Hioe. Analytic solutions for three-state systems with overlapping pulses. *Phys. Rev. A (3)*, 42(3):1522–1531, 1990.
- [Cha12] Thomas Chambrion. Periodic excitations of bilinear quantum systems. *Automatica*, 48(9):2040–2046, 2012.

- [CMSB09] Thomas Chambrion, Paolo Mason, Mario Sigalotti, and Ugo Boscain. Controllability of the discrete-spectrum Schrödinger equation driven by an external field. *Ann. Inst. H. Poincaré Anal. Non Linéaire*, 26(1):329–349, 2009.
- [D’A08] Domenico D’Alessandro. *Introduction to quantum control and dynamics*. Applied Mathematics and Nonlinear Science Series. Boca Raton, FL: Chapman, Hall/CRC., 2008.
- [EAGK96] R. El Assoudi, J. P. Gauthier, and I. A. K. Kupka. On subsemi-groups of semisimple Lie groups. *Ann. Inst. H. Poincaré Anal. Non Linéaire*, 13(1):117–133, 1996.
- [EP09] Sylvain Ervedoza and Jean-Pierre Puel. Approximate controllability for a system of Schrödinger equations modeling a single trapped ion. *Ann. Inst. H. Poincaré Anal. Non Linéaire*, 26:2111–2136, 2009.
- [GB82] J.-P. Gauthier and G. Bornard. Controlabilité des systèmes bilinéaires. *SIAM J. Control Optim.*, 20(3):377–384, 1982.
- [JK81] V. Jurdjevic and I. Kupka. Control systems on semisimple Lie groups and their homogeneous spaces. *Ann. Inst. Fourier (Grenoble)*, 31(4):vi, 151–179, 1981.
- [JS72] Velimir Jurdjevic and Héctor J. Sussmann. Control systems on Lie groups. *J. Differential Equations*, 12:313–329, 1972.
- [Mir09] Mazyar Mirrahimi. Lyapunov control of a quantum particle in a decaying potential. *Ann. Inst. H. Poincaré Anal. Non Linéaire*, 26(5):1743–1765, 2009.
- [MS10] Paolo Mason and Mario Sigalotti. Generic controllability properties for the bilinear Schrödinger equation. *Communications in Partial Differential Equations*, 35:685–706, 2010.
- [Ner09] Vahagn Nersesyan. Growth of Sobolev norms and controllability of the Schrödinger equation. *Comm. Math. Phys.*, 290(1):371–387, 2009.
- [Ner10] Vahagn Nersesyan. Global approximate controllability for Schrödinger equation in higher Sobolev norms and applications. *Ann. Inst. H. Poincaré Anal. Non Linéaire*, 27(3):901–915, 2010.
- [NN12] Vahagn Nersesyan and Hayk Nersisyan. Global exact controllability in infinite time of Schrödinger equation. *J. Math. Pures Appl. (9)*, 97(4):295–317, 2012.
- [PS10] Yannick Privat and Mario Sigalotti. The squares of the Laplacian-Dirichlet eigenfunctions are generically linearly independent. *ESAIM Control Optim. Calc. Var.*, 16(3):794–805, 2010.

- [SH06] T. Seideman and E. Hamilton. Nonadiabatic alignment by intense pulses: concepts, theory and directions. *Adv. At. Mol. Opt. Phys.*, 52:289, 2006.
- [SKA<sup>+</sup>04] D. Sugny, A. Keller, O. Atabek, D. Daems, C. Dion, S. Guérin, and H. R. Jauslin. Reaching optimally oriented molecular states by laser kicks. *Phys. Rev. A*, 69:033402, 2004.
- [SS03] H. Stapelfeldt and T. Seideman. Aligning molecules with strong laser pulses. *Rev. Mod. Phys.*, 75:543, 2003.
- [Tur00] Gabriel Turinici. On the controllability of bilinear quantum systems. In M. Defranceschi and C. Le Bris, editors, *Mathematical models and methods for ab initio Quantum Chemistry*, volume 74 of *Lecture Notes in Chemistry*. Springer, 2000.
- [VHBB01] NV Vitanoc, T Halfmann, Shore BW, and K Bergmann. Laser-induced population transfer by adiabatic passage techniques. *Annual review of physical chemistry*, 52:763–809, 2001.